

	From the INTERNATIONAL BUREAU
РСТ	To:
NOTIFICATION OF ELECTION (PCT Rule 61.2) Date of mailing (day/month/year)	Commissioner US Department of Commerce United States Patent and Trademark Office, PCT 2011 South Clark Place Room CP2/5C24 Arlington, VA 22202 ETATS-UNIS D'AMERIQUE
18 January 2001 (18.01.01)	in its capacity as elected Office
International application No. PCT/FI00/00397	Applicant's or agent's file reference 991111 WO
International filing date (day/month/year) 04 May 2000 (04.05.00)	Priority date (day/month/year) 14 May 1999 (14.05.99)
Applicant NYMAN, Bror et al	
in a notice effecting later election filed with the Inter 2. The election X was was not	r 2000 (29.11.00) rnational Bureau on:
Rule 32.2(b).	date or, where Rule 32 applies, within the time limit under
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nestor Santesso

Telephone No.: (41-22) 338.83.38

Facsimile No.: (41-22) 740.14.35

1001906PGT/F100/00397

Copy for the designated Office (DO/US)

ATENT COOPERATION TREETY

10019967

PCT	То:				
NOTIFICATION OF THE RECORDING OF A CHANGE (PCT Rule 92bis.1 and Administrative Instructions, Section 422) Date of mailing (day/month/year) 13 December 2000 (13.12.00)	OUTOKUMPU OYJ Intellectual Property Management P.O. Box 27 FIN-02201 Espoo FINLANDE				
Applicant's or agent's file reference 991111 WO	IMPORTANT NOTIFICATION				
International application No. PCT/F100/00397	International filing date (day/month/year) 04 May 2000 (04.05.00)				
1. The following indications appeared on record concerning: the applicant the inventor	the agent the common representative				
Name and Address OUTOKUMPU OYJ Patent Services P.O. Box 27 FIN-02201 Espoo Finland	State of NationalityState of ResidenceTelephone No.358-9-4211Facsimile No.358-9-4212978Teleprinter No.				
2. The International Bureau hereby notifies the applicant that the the person the name X the add Name and Address					
OUTOKUMPU OYJ Intellectual Property Management P.O. Box 27 FIN-02201 Espoo Finland	Telephone No. 358-9-4211 Facsimile No. 358-9-4212978 Teleprinter No.				
3. Further observations, if necessary:					
 A copy of this notification has been sent to: X the receiving Office the International Searching Authority the International Preliminary Examining Authority 	X the designated Offices concerned the elected Offices concerned other:				
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Aino Metcalfe Telephone No.: (41-22) 338.83.38				

Form PCT/IB/306 (March 1994)

. .



PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT 11 JUN 2001

(PCT Article 36 and Rule 70)

WIFO PCT

Applicant's or agent's file reference	FOR FURTHER ACTION		ation of Transmittal of International Examination Report (Form PCT/IPEA/416)
991111 WO			Priority date (day month year)
International application No.	International filing date (day mont	in year)	, , , ,
PCT/FI00/00397	04.05.2000	······	14.05.1999
International Patent Classification (IPC) of			
B01D 11/04, C22B 3/26	// C22B 15:00		
Applicant			
Outokumpu Oyj et al			
 This international preliminary exa Authority and is transmitted to the 	mination report has been prepared been prepared been prepared been applicant according to Article 36.	by this Inter	national Preliminary Examining
2. This REPORT consists of a total	of <u>4</u> sheets, includin	g this cover	sheet.
been amended and are the l	nied by ANNEXES, i.e., sheets of t pasis for this report and/or sheets con a 607 of the Administrative Instruct	ntaining rec	on, claims and/or drawings which have tifications made before this Authority he PCT).
These annexes consist of a total of	f sheets.		
3. This report contains indications re	lating to the following items:		
I Basis of the report			
II Priority			
III Non-establishment o	f opinion with regard to novelty, inv	ventive step	and industrial applicability
IV Lack of unity of inve	ntion		
	inder Article 35(2) with regard to not tions supporting such statement	ovelty, inve	ntive step or industrial applicability;
VI Certain documents c	ted		
VII Certain defects in the	international application		
VIII Certain observations	on the international application		
	. - -		
	<u> </u>		

Date of submission of the demand	Date of submission of the demand		
29.11.2000		15.05.2001	
Name and mailing address of the IPEA/SE		Authorized officer	
Patent- och registreringsverket Pom 5055	Tele≭ 17978		
S-102 42 STOCKHOLH	FATOREG-S	Lars Ekeberg/js	
Facsimile No. 08-667 72 88		Telephone No. 08-782 25 00	
Facsimile No. 08-667 72 88	009	Telephone No. 08-782 25 00	

Form PCT/IPEA/409 (cover sheet) (January 1998)

1

.U

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

e.

International application No.

PCT/FI00/00397

I. Basis of the report
1. With regard to the elements of the international application:*
the international application as originally filed
the description:
pages . as originally filed
pages filed with the deman
pages, filed with the letter of
the claims:
pages as originally file
pages, as amended (together with any statement) under article 1
pages, filed with the letter of
the drawings:
pages as originally filed pages filed with the deman
pages filed with the letter of
the sequence listing part of the description:
pages as originally file
pages . filed with the deman
pages, filed with the letter of
the international application was filed, unless otherwise indicated under this item. These elements were available or furnished to this Authority in the following language which is the language of a translation furnished for the purposes of international search (under Rule 23.1(b)). the language of publication of the international application (under Rule 48.3(b)). the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/ or 55.3).
3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
contained in the international application in written form.
filed together with the international application in computer readable form.
furnished subsequently to this Authority in written form.
furnished subsequently to this Authority in computer readable form.
 The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished. The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
the description, pages
the claims, Nos.
the drawings, sheet/fig
5. This report has been established as if (some of) the amendments had not been made, since they have been considered to get beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).**
 Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).
** Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

Form PCT/IPEA/409 (Box I) (January 1998)

.

	,					
			MAN ATION DEPORT	International application No.		
	INTERNATIONAL PRELIM	IINARY EXA	MINATION REPORT	PCT/FI00/00397		
V.	Reasoned statement under Articl citations and explanations support	e 35(2) with r rting such sta	egard to novelty, inventive s tement	step or industrial applicability;		
	Statement					
	Novelty (N)	Claims	1-18		YES	
		Claims			_ NO	
	Inventive step (IS)	Claims	1_18		YES	
	inventive step (18)	Claims			_ NO	
					YES	
	Industrial applicability (IA)	Claims Claims			$-\frac{110}{NO}$	
		Channe				
	Citations and explanations (Rule 7	0.7)				
		adina ta	a_{1-18} r	elates to a method f	or	
	extraction of con	per fro	m an aqueous	solution containing	a	
	large amount of	sulphat	es in liquid-	liquid solution. T	he	
	viscosity of the ex	ktractic	on solution lie	s between 3 and 11 c	Ρ.	
	The between the ex	tractic	on solution and	the aqueous soluti	on	
	is situated between	n 0.7 ar	nd 1.0.			

The following documents are, among others, cited in International Search Report: D1: GB 2 117 666 A D2: US 4,221,658 A

D3: US 5,662,871 A D4: US 5,185,081 A

Of these documents D1 and D2 were considered to be of particular relevance, while D3 and D4 only were considered to represent the general state of the art, and are therefore not discussed in this report. However, the importance of D1 and D2 have been re-evaluated. They are now only considered to represent the general state of the art.

From D1, a method for hydrometallurgical extraction of copper is known. The ratio between the extraction solution and the aqueous solution is preferably situated around 1.0 (claim 9).

Another extraction method is known from D2. In both D1 and D2 the preferred volume ratio is situated between 0.2 and 5. Nothing is, on the other hand, said about the viscosity, in neither of the documents. It is not suggested that an augmentation of the viscosity could have a positive influence on the extraction.

. . . / . . .

the

.

•

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00397

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Box V (I)

Although it is difficult to estimate the viscosity of the solutions used in D1 and D2, the invention is considered to involve an inventive step with regard to both of these documents. Claims 2 -18 are dependent on the first claim, hence, these claims are also considered to possess an inventive step.

In view of the argument stated above, the invention as a whole is novel and considered to involve an inventive step. It is also considered to fulfil the criteria of novelty and industrial applicability.



Å,

10,

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau

•



		(11) International Publication Number: WO 00/6953
B01D 11/04, C22B 3/26 // 15:00	A1	(43) International Publication Date: 23 November 2000 (23.11.00
1) International Application Number: PCT/I 2) International Filing Date: 4 May 2000	F100/0039	BR, BY, CA, CH, CN, CU, CZ, DE, DK, FF, FS, FI, GF
) Priority Data: 991111 14 May 1999 (14.05.99)		 KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, Si SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA ZW, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ TM), European patent (AT, BE, CH, CY, DE, DK, ES, FJ
) Applicant (for all designated States except US OKUMPU OYJ [FI/FI]; Riihitontuntie 7, FIN-02 (FI).): OU 2200 Espe	FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
 Diventors; and Diventors/Applicants (for US only): NYMAN, Br Ruispolku 1, FIN-28450 Vanha-Ulvila (Fl). HU Stig-Erik [FI/FI]; Sitomantie 1, FIN-28360 LILJA, Launo [FI/FI]; Liisankatu 19 A, FIN-2 (FI). LINDELL, Esa [FI/FI]; Tähtisentie 14, FI Vanha-Ulvila (FI). EKMAN, Eero [FI/FI]; 1 7 A, FIN-28100 Pori (FI). LYYRA, Juhar Kalastajankuja 1 E, FIN-02230 Espoo (FI). KN Raimo [FI/FI]; Kalastajankuja 1 D, FIN-02230 F PEKKALA, Pertti [FI/FI]; Vehaksentie 45 B, F Espoo (FI). 	LTHOLN Pori (FI 28100 Po FIN-2845 Itälinjakat ni [FI/FI UUSISTO 3spoo (FI	A, amendments.). ri 0 uu];];
) Agent: OUTOKUMPU OYJ; Patent Services, P.O FIN-02201 Espoo (FI).) Title: A METHOD FOR EXTRACTING COPPER		
	-6	

The invention relates to a method for extracting copper in liquid-liquid solvent extraction from aqueous solution with a high sulphate content, by raising the viscosity of the extraction solution and by dispersing the aqueous solution into drops, achieving a dense drop aggregation. The viscosity of the extraction solution may be raised either by increasing the content of the actual extractant, the extraction reagent, in the extraction solution or by using a diluting agent with a higher viscosity than that of the diluting agent normally used. By raising the viscosity of the extraction solution the mixing durability of the extraction dispersion can be increased and resulting of that the amount of residual drops is decreased. Other advantages are that the extraction solution flow of the extraction process decreases in relation to the flow of the aqueous solution acting as the copper source and that the size of the extraction equipment needed is reduced.

	· · · · · · · · · · · · · · · · · · ·		FOR THE PURPOS	ES OF IN	FORMATION ONLY	· .	
		States pa	rty to the PCT on the fro	ont pages o	f pamphlets publishing in	ternation	al applications under the PC
L	Albania	ES	Spain	LS	Lesothe	SI	Slovenia
M	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
Т	Austria	FR	France	LU	Luxembourg	SN	Senegal
U	Australiza	GA	Gabor:	. LV	Larvia	SZ	Swaziland
Z	Azerbaijan	GB	United Kingdom	мс	Monaco	TD	Chad
A.	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
B	Barbados	GH	Ghana	́ МG	Madagascar	ТJ	Tajikistan
E.	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
F	Burkina Faso	GR	Greeca	• .	Republic of Macedonia	TR	Turkey
G	Bulgaria	HU	Hungary	ML	Mali	ŤŤ	Trinidad and Tobago
r –	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
R	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
r	Belarus	1S	iceland .	MW	Malawi	US	United States of America
A.	Canada	IT	Italy	імх	Mexico	UZ	Uzbekistan
F	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
G	Солдо	KE	Кепуа	· NL	Netherlands	· YU ·	Yugoslavia
H	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
E	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		•
м	Cameroon		Republic of Korea	PL	Poland		
N	China	KR	Republic of Korea	PT	Portugal		
U	Cuba	КZ	Kazakstan	RO	Romania		
z	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
E	Germany	u	Liechtenstein	SD	Sudan		
к	Denmark	LK	Sri Lanka	SE	Sweden		
E	Estonia	LR	Liberia	SG	Singapore		

ج•.

.

٢.

12/101/2

A METHOD FOR EXTRACTING COPPER FROM AN AQUEOUS SOLUTION

10/019967

PCT/FI00/00397

JC13 Reg'd PCT/PTO

The present invention relates to a method for extracting copper in liquid-liquid solvent extraction from aqueous solutions with a high sulphate content, by raising the viscosity of the extraction solution and by dispersing the aqueous 5 solution into drops, achieving a dense drop aggregation. The viscosity of the extraction solution may be raised either by increasing the content of the actual extractant, the extraction reagent, in the extraction solution or by using a diluting agent with a higher viscosity than that of the diluting agent normally used. By raising the viscosity of the extraction solution the mixing durability of 10 the extraction dispersion can be increased and resulting of that, the amount of residual drops is decreased. Other advantages are that the extraction solution flow of the extraction process decreases in relation to the flow of the aqueous solution acting as the copper source and that the size of the extraction equipment needed is reduced. 15

Dilute aqueous solutions form when poor copper ores are leached directly. The copper content of such solutions is usually of the order of 1 - 4 g/l Cu. In addition neutral salts often accumulate in the solution, mainly aluminium and magnesium sulphates. Although the copper content does not rise above 1.5 20 g/l, the sulphate content may rise above 40 g/l, to between 40 and 120 g/l. Some of the sulphate may originate from the ore or the possible use of seawater. In the extraction process the aqueous solution is in a cycle between the extraction and the leaching and thus gradually accumulates the salts which raise the viscosity. Neutral salts can easily cause a viscosity increase 25 harmful to the aqueous solution, even 3 cP, which also disturbs the dispersing of the aqueous and extraction solutions and results in high amounts of residual drops. In particular when dispersion is desired where the organic solution is continuous and the wat r in drops, an incr as d viscosity in the aqueous solution can make it difficult to achi v such a dispersion. Previously 30

PCT/FI00/00397

4

:2

WO 00/69538

the increas d viscosity caused by neutral salts and the resulting disadvantages were not taken into account.

In copper extracting processes a mixed organic extraction solution and 5 aqueous solution is generally used in the ratio of O/A (organic/aqueous) 1.0 -1.2. Present-day copper extracting processes usually follow recommendations given by extractant manufacturers, according to which the organic and aqueous solution of the extraction O/A ratio at all extraction stages of the extraction process should be of the order of 1.0, and the extractant content 10 raised to 3.3 - 4.2 vol.% per every gram of copper, which comes in the direction of flow of the first extraction stage of extraction. In practice this means that if the Cu content of the aqueous solution is 1.5 g/l, the extractant content is maximum 6.3 vol.% according to the recommendations. Generally, when the amount of copper in the solution increases, the amount of extractant 15 decreases relatively. The type of extractant is a chelating copper complexing agent, usually hydroxyoxyme, which forms a strong complex with copper, and one fact affecting the progress of copper extraction is how much extractant is present in relation to the amount of copper to be extracted.

20 Generally, alifatic or aromatic hydrocarbons, kerosenes, with a distillation range between 190 – 245 °C are used as the diluting agent for the copper extractant. The viscosity of these substances is usually below 2 cP, and for aromatics even below 1.5 cP. It is also possible to us mixtures of aromatic and alifatic hydrocarbons as the diluting agent, where the aromatic content of the 25 mixture is around 20 – 30 vol.%.

As previously stated, in copper extraction it is difficult to get a dispersion of an aqueous solution with a high sulphate content, minimum 40 g/l, where the organic phas is continuous and the aqueous s lution in drops, although this 30 is ssential in order to improve extraction performance. According to the pr s nt invention, the viscosity of the extraction solution is now raised to the

5

٦,`

PCT/FI00/00397

3

ه جنه ه و د این د ه د و د و

area of 3 –11 cP, and this takes plac ither by raising the extractant content or by using a diluting agent with a high viscosity in the extraction solution. In addition to this, that the organic phase has been made continuous, the method has proved to have many other advantageous consequences. The essential features of the invention will become apparent in the attached patent claims.

A rise in the viscosity of the extraction solution clearly raises the mixing durability of the extraction dispersion. In this connection a mixing-durable dispersion means a dispersion where no drops below 0.2 mm appear when 10 ٠. the mixing intensity is max. 0.15 kWh/m³ in a mixing volume of 50 m³. Volume-specific mixing power is dependent on the mixing volume so that the power required decreases slightly as the volume increases. Obviously the mixing itself also affects mixing durability. The mixers described in US patent 5,185,081 have been settled on to use in the method according to the present 15 👘 invention. These mixers have a double helix, which helps to avoid locally increasing shear rate forces and the small drops generated as a result. When the viscosity of the organic phase has been raised according to the invention and the extraction dispersion made heavier and this dispersion combined with a very smooth, thoroughly uniform mixing of controlled intensity in the mixing 20 area, the conditions are achieved where an evenly distributed mixing energy is not sufficient to attain a turbulence to form droplets. An evenly attenuated mixing creates a dispersion where the drop size is uniform and which thus • possesses good separation characteristics. Since the amount of residual drops is small, the extraction result is clearly improved. 25

In addition to the increase in viscosity of the extraction solution, another key factor is the mixing ratio of the solutions. The denser the drop aggregation, th heavier and simultane usly more mixing-durable the dispersion. The most advantag ous result is obtained when a dispersion is formed, where the extraction solution is continuous and the amount of water drops is raised.

:

: Դ

4

When the viscosity of the extraction solution is raised, it has been found that an extraction solution with a higher viscosity is better able to keep a larger amount of the aqueous solution than normal inside it as drops. In the method according to our invention it is possible to lower the O/A ratio to between 0.7 -1.0 without endangering the continuity of the extraction solution. In practice, this means that the extraction solution flow can be reduced in relation to the copper-containing feed solution (the aqueous solution) by the amount previously described. At the same time the extractant content of the extraction solution is increased to the extent that the mass flow of the extraction solution stays unchanged or increases a little. Thus the viscosity of the extraction solution can be reised successfully.

The factor by which the extractant content is raised compared with the normal recommendation in the method according to the present invention, varies between 1.2 - 5, and is preferably between 1.5 - 3. When very dilute 15 copper-containing feed solutions with max. 2 g/l of copper are being treated, the factor may always rise to 5 i.e. according to our invention the extractant content would then be of the order of 7 - 25 vol.%, preferably 15 - 25 vol. %. When the feed solution copper content is between 2 - 4 g/l, the preferred extractant content is in the range of 15 - 30 vol.%. Generally, however, the 20 extractant content does not increase above a content of 30% by volume. The viscosity of the extraction solution in this case rises to between 3 - 7 cP, which is enough to raise it to a clearly higher level than the viscosity of the aqueous solution. Normally, the aim is to achieve an O/A viscosity ratio of between 1.2 - 3, preferably 1.5 - 2. According to the invention, when 25 extracting dilute copper solutions the extractant content in the extraction solution is presently set in the range of 7 - 30 vol.%, preferably 15 - 30 vol.%.

30

R garding aqueous solutions containing over 4 g/l of copp r, even an rdinary extractant content in the extraction solution giv s a fairly good result. For these solutions, the use of an extractant factor of 1.2 – 2.0 times the

10

÷

5

10

15 ·

PCT/FI00/00397

5

recommendation improves the mixing durability of the dispersion. With the method according to the invention, however, it is possible to raise the extractant content in the extraction solution to 25 - 50 vol.%, when the copper content of the aqueous solution is 4 - 8 g/l and even up to 40 - 70 vol.% if the copper content of the solution is over 8 g/l. The viscosity of the extraction solution can also be raised partly or wholly with the use of a diluting ag nt. The distillation range and viscosity of the diluting agents generally used was mentioned earlier as being rather low. If other diluting agents are used, this can also raise the viscosity of the extractant. Alifatic hydrocarbon products can be chosen with a distillation range in the range of 220 - 275 °C or 240 - 270 °C, and the viscosity of these substances measured at a temperature of +25 °C is 2.7 or 3.2 cP. If it is desired to use aromatic hydrocarbons, the viscosity of hydrocarbons with a distillation span of 230 - 290 °C is about 3 cP. It is also possible to use mixtures of alifatic and aromatic hydrocarbons.

When treating dilute aqueous solutions containing less than 4 g/l of copper, there is a possibility in our invention of using hydrocarbon compounds that boil at a high boiling range as the diluting agent. The use of a diluting agent to increase viscosity is preferred since the diluting agent is always cheaper than the actual extractant. The proportion of diluting agent in the extraction solution can be between 30 - 93%. It is easier to achieve the required rise in viscosity without the density of the extraction solution increasing significantly with alifatic hydrocarbons. The use of alifatic hydrocarbons is also recommended for reasons of industrial hygiene.

25

• :

...

30

20

It was mentioned above that when raising the viscosity of the extraction solution it is possible to decrease the external pumping of the extraction solution coming to the extraction stage from outside. If the rise in viscosity takes place with an xtraction solution diluting agent, it is not possible to decreas pumping. On the other hand, wh n viscosity is rais d with an extractant, external pumping of the extraction solution can be reduced

20



Ĕ.

9¥.

6

significantly compared with th amount of copper-containing aqueous solution being conveyed to the extraction stage. If viscosity is raised both by increasing the extractant content and by using the aforementioned diluting agent, the amount of external pumping decreases in the same degree as the extractant content is increased.

5

The method according to our invention is described in the attached drawings, where

Figure 1 shows a schematic view of the equipment used in the method of the 10 present invention.

Figure 2 shows a stage calculation of the prior art, where the copper content of the aqueous solution (PLS = pregnant leach solution) coming to the extraction stage is 1.5 g/l and the extractant content of the extraction solution is 5 vol. % Acorga M 5640,

Figure 3 shows a stage calculation according to the present invention, where 15 the copper content of the PLS is 1.5 g/l and the extractant content of the extraction solution is 15 vol. % Acorga M 5640,

Figure 4 shows a stage calculation according to the present invention, where the copper content of the PLS is 1.5 g/l and the extractant content of the extraction solution is 25 vol. % Acorga M 5640,

Figure 5 shows a stage calculation according to the prior art, where the copper content of the PLS is 3.0 g/l and the extractant content of the extraction solution is 8.5 vol. % Acorga M 5640,

Figure 6 shows a stage calculation according to the present invention, where the copper content of the PLS is 3.0 g/l and the extractant content of the 25 extraction solution is 15 vol. % Acorga M 5640,

Figure 7 shows a stage calculation according to the present invention, where the copper content of the PLS is 3.0 g/l and the extractant content of the xtraction solution is 25 vol. % Acorga M 5640,

7

Figure 8 shows a stage calculation according to the present invention, where the copper content of the PLS is 6.5 g/l and the extractant content of the extraction solution is 22 vol. % Acorga M 5640,

Figure 9 shows a stage calculation according to the present invention, wher

- 5 the copper content of the PLS is 6.5 g/l and the extractant content of the extraction solution is 30 vol. % Acorga M 5640,
 - Figure 10 shows a stage calculation according to the present invention, where the copper content of the PLS is 6.5 g/l and the extractant content of the extraction solution is 40 vol. % Acorga M 5640,
- 10 Figure 11 shows a stage calculation according to the present invention, where the copper content of the PLS is 2.5 g/l and the extractant content of the extraction solution is 40 vol. % LIX 984N, and

Figure 12 shows a stage calculation according to the present invention, where the copper content of the PLS is 32 g/l and the extractant content of the extraction solution is 50 vol. % Acorga M 5640.

Figure 1 describes a copper extraction process for treating dilute copper solutions. The process consists of two extraction stages, E1 and E2, one extraction solution washing stage W and one extraction solution stripping stage S. Both the extraction stages and the washing and stripping stag s consist of a mixing section 1, a settler 2, and a pump 3 used to transfer the dispersion. The mixing section has at least one mixer, which is preferably equipped with the mixing devices described earlier. The principles of th extraction stages are the types described in e.g. WO patent application publications 97/40899, 97/40900, 97/40901 and 97/41938.

.

30

25

15

20

As usual, the extraction functions on a counterflow principle, whereby aqueous solution 4 comes first to extraction stage E1 and extraction solution 5 to stage E2. The aqueous solution exiting the final extraction stage E2, raffinate 6, is fed back to ore leaching, and copper-enrich d extraction solution 7 is fed from E1 to washing W and stripping S. In practice, the

PCT/FI00/00397

t

.

8

xtraction solution is circulated via storage tanks. L an lectrolyte 8 is fed from electrolysis to the stripping stage where the copper contained in the organic phase is extracted. The aqueous solution 9 containing copper sulphate exiting the stage goes as rich electrolyte to electrowinning and the stripped organic phase 5 is circulated back to extraction stage E2.

Figure 1 shows how considerably the size of the washing and stripping stages of the extraction process is reduced when an extractant is used according to the invention to raise the viscosity of the extraction solution. In fact the reduction is in direct ratio to the external extraction solution pumping, because the mixer-settlers in question are dimensioned directly with the solution flows in all respects, pumping, mixing and solution separation.

Therefore, in cases where the extractant content is raised for example to double the amount normally used, and external extraction solution pumping is correspondingly decreased to half the normal flow, the mixer and settler volumes of the washing and stripping stages are halved. The actual extraction stages E1 and E2 remain almost their earlier size and the same external extraction solution pumping goes through them, but the extraction solution can be circulated within the stages in order to maintain extraction solution continuity. The extraction solutions flow through each stage of the extraction equipment at essentially the same time. As mentioned above, the O/A mixing ratio of the solutions may be reduced according to the method of the invention to below 1 to a value between 0.7 - 1.0, and the size of the extraction stages equipment can be reduced correspondingly.

When estimating the effect of our invention on the size of the extraction equipment, it should be noted that Fig. 1 is only indicative of the relative size of the extraction stag s and that of the washing and stripping stages. There ar often two stripping stag s in an extraction plant and in some cases also two washing stages. Then the savings made by reducing the size of the

10

15

5

20

25

5

9

equipment ar correspondingly greater. The amount of extraction solution inside the extraction plant is also reduced correspondingly even if the changes in the amount of extractant itself are not large, since the content of extractant in the extraction solution has been raised. In certain cases it is expedient even to raise the amount of extraction agent circulating in the process, so that the advantages described in the method can be achieved in full measure.

The method according to our invention provides the opportunity to treat difficult impurities such as copper ore containing chloride, nitrate or manganese in an economical way. In particular, ores containing a lot of iron are generally problematic, because iron increases the transfer of the above-mentioned impurities to the electrolyte via the extraction solution. This results in a situation where it is even more important than before to prevent the transfer of said impurities first to the extraction solution with the unseparated drops of aqueous solution from extraction stage E1 to washing stage W and from there on to stripping stage S.

.1:

According to our invention it is now possible to use equipment that is smaller than usual in the washing stage, but as it is known on the other hand, a prolonged settling time in the washing stage (larger settler) improves the separation of impurities. Now it is possible to enlarge the washing stage, in particular its settler section in relation to the extraction solution flow used, for instance the size of a settler according to the conventional method without increasing costs and to achieve better separation of impurities than before. In practice this means that in the washing and stripping stages the mixing and separating times are longer, i.e. the solutions flow through them more slowly than through the actual extraction stages. With this system our method offers the possibility for flexible, case-specific dim nsioning.

10

When poor copper ores are processed by direct leaching, the result, as stated above, is an aqueous solution with a copper content in the range of 1 - 4 g/l, and in addition neutral salts accumulate in the solution. The sulphate content of the solution may rise to between 40 - 120 g/l, which causes a rise in the viscosity of the aqueous solution, but on the other hand, sulphate has the benefit of acting as a pH buffer when using copper extraction in the pH range of 0.8 - 2.2. In other words it improves the equilibrium of the copper extraction and makes more copper transfer to the extraction solution.

10 Example 1

5

15

A series of tests were carried out, which show that the separation of th organic solution and the aqueous solution from each other improves when the viscosity of the organic phase is raised by increasing the extractant content in copper extraction according to our invention. Table 1 presents the composition of the extraction solution and the results obtained.

The aqueous solution was made using ion-exchanged water, copper sulphat and sulphuric acid. The copper content of the solution was 2 g/l, the sulphate content 52 g/l and the pH 1.8. The extraction solution was prepared by mixing the commercial extractants shown in the table in different proportions with a commercial kerosene solution D70 as diluting agent. Mixing contact was made between the extraction solutions and the copper sulphate solution (aqueous solution) at room temperature and in the O/A phase ratio of 1.0, thereby obtaining the copper content values of the solutions in the table. After mixing all the solutions were recovered and stored for two weeks before the actual mixing tests. This ensured that the extraction solutions in particular corresponded to the solutions used in normal extraction, without th drawbacks of new extraction solutions.

30 A double helix agitator as described in US patent 5,185,081, with a diameter of 152 mm and height of 174 mm was used in the mixing tests. The mixer itself

PCT/FI00/00397

11

was a flat-bottomed cylinder with a diameter of 214 mm and effectiv solution depth also of 214 mm. The cylinder was equipped with four baffles positioned on the frame of the cylinder, with a width of 18 mm and at a distance of 3.5 mm from the inner surface of the cylinder.

The mixing contact itself was made at room temperature and in the O/A phase ratio of 1.0 so that the extraction solution was continuous in all tests and the aqueous solution in drops. The revolution speed of the mixer was 220 rpm and the duration of mixing was 3 minutes in all tests. In all tests each extraction

solution was mixed with a new batch of the aqueous solution. After mixing th 10 solutions were made to separate by the effect of gravity. 15 minutes after mixing the amount of residue solution in each of the separated solutions was determined. The drop residues (entrainment levels) are shown in Table 1, where A/O means water in the extraction solution and O/A means organic phase drops in the aqueous solution. 15

Table 1

lest.	Extr.sol.				Viscos.	Cu/oxtr.eol.	Residual	lrops
	Extractant		Dil. agent '~	· · · ·	· · ·	1 1 1 K 1 1	. A/O	0/A ;
	· · · · ·	til%		ซ์ไ %	cP	<u>م</u> و	ppm	ppm
1 ~	Acorga M5640	5	D70	95	2,7	2	500	90
2	Acorga M5640	8,5	D70	91,5	3	3,5	450	.70
3	Acorga M5640	15	⁻ D70	85	3,3	6,2	150	40
4	Acorga M5640	25	D70	75	4,2	7,4	100	25
5	Acorga M5640	30	D70	70	4,9	13,7	150	25
6	LDC984N	40	D70	60'	6,1	19,8	50	15
7	Acorga M5640	50	D70	50	8,2	20,1	50	12

20

÷

٠,

The tests show that raising viscosity by increasing the extractant (extraction reagent) content clearly decreases the amount of residual drops in the settled solutions.

12

Example 2

An aqueous solution was prepared with a copper content of 1.5 g/l, sulphat content of 50 g/l and pH of 1.8. Three different extraction solutions were also prepared:

5	1.	Acorga M5640	5.0 vol%
		D70	95 vol%
	2 .	Acorga M5640	15.0 vol%
		D70	85 vo!.~%
•	Э.	Acorga M5640	25.0 vol%
10		C70	75 vol%

The first solution represents an extraction solution according to the prior art.

Extraction equilibriu.n curves EEQ and stripping equilibrium curves SEQ
shown in Figs 2, 5 and 4 were defined for the extraction solutions and aqueous solutions in question with the method used by experts in this field. Diagram 2 shows the prior art, diagrams 3 and 4 the method according to this invention. Next, making use of the equilibrium data in question, an extraction calculation was made for a copper extraction process with two extraction stages functioning on the counterflow principle and two stripping stages. Th calculation was made on the basis of the McCabe-Thiele method, familiar t specialists in the field. The extraction and stripping stages reach as far as the equilibrium curve, because the stage efficiency is very high when using for instance the equipment described in WO patent publications.

25

The three stage calculations presented in the example show that the copper extraction yield remains at a good level and almost unchanged, even though the external pumping of the extraction solution is reduced. The copper contents of the raffinate are in all cases 0.2 - 0.4 g/l. The lowest content is obtained by raising the extractant content to 15%, where by the external pumping of the extraction solution can be reduced to 35% of the PLS

5

·...

25

:

13

(pregnant leach solution) feed i.e. copper-containing aqueous solution feed. It is apparent from the stage calculation in question that the extraction equilibrium remains good in extraction conditions (the EEQ curve rising steeply when the Cu content of the aqueous solution is under 0.5 g/l) over its extraction solution copper content level, set for the extraction solution after the second stripping stage S2 (dotted line BO, e.g. 3.0 g/l in Figure 3).

Another essential factor is that the stripping equilibrium allows the making of strong copper electrolyte when the copper content of the extraction solution can be lowered sufficiently. This means the level where the extraction 10 equilibrium is still rising sharply in an aqueous solution Cu content of under 0.5 g/l, as stated earlier. The stage calculation reveals that with the method according to the present invention, a significant improvement is achieved in the copper content of the electrolyte going to copper electrolysis. With two stripping stages the electrolyte was made almost saturated as regards 15 copper sulphate.

In different stage calculations the copper electrolyte developed as follows: in a normal copper process (extractant content 5 vol.%) the copper content of the "poor" electrolyte (LEL = lean electrolyte) coming to the washing stage is . 20 to be kept as low as 34 g/i and in the "rich" electrolyte (REL = rich electrolyte) the content may rise to the value of 42.5 g/l. In the present method the corresponding values are 36 g/l and 50 g/l when using an extractant content of 15 vol. % and 36 g/l and 51.5 g/l when using an extractant content of 25 vol. %.

In the method according to the present invention a smaller amount than usual of extraction solution is circulated in relation to the PLS solution. . Likewise the lectrolyt circulation is correspondingly much smaller. In order to describe the information included in the stage calculations the circulation 30 of the solutions can be checked for instanc on th basis of diagram 3. The

stage calculation is in two parts: extraction on the left and stripping on the right. The solution compositions of the different stages can be seen at the intersection points of the stages and the equilibrium curves. For example, in extraction stage E1 the Cu content of the aqueous solution decreases from the PLS content of 1.5 g/l to 0.6 g/l and the Cu content of the extraction solution rises from the E2 content of 4.2 g/l to 6.7 g/l. In stripping stage S1 the extraction solution on the other hand falls from an LO (loaded organic) value of 6.7 g/l to 4.2 as the Cu content of the copper electrolyte rises from

40.4 g/l to 50.0 g/l. The Cu content of the extraction solution falls further to a BO (barren organic) value of 3.0 in stripping stage S2, from where the

extraction solution moves on to extraction stage E2 of the extraction.

10 [·]

5

The important points in said stage calculations are the so-called operating lines which indicate the contents in which the solutions touch each other when entering or leaving the first extraction and stripping stages E1 and S1 and the final extraction and stripping stages E2 and S2 and in between said stages. From the nature of the stage calculations it follows that the gradient of the operating lines indicate the external solution pumping i.e. the ratio of PI_S and extraction solution flows in extraction as well as the ratio of electrolyte and extraction solution flows in stripping. It has been possible to calculate from the external pumping ratios how much the electrolyte circulation is reduced with our method in relation to the amount of PLS flow.

Certain figures characteristic of our invention have been assembled in Table 2, when the extractant contents of the extraction solution are 15 and 25 vol.% and these figures are compared with figures for conventional copper extraction, where the extractant content is 5 vol. %. The copper content of the aqueous solution (PLS) is 1.5 g/l in all cases. The extractant is Acorga M5640 and the diluting agent kerosen D70. The temperature of the 30 extraction solution is 18 °C.

15

Tabl 2

Quantity	Kuva 2	Kuva 3	Kuva 4
Extractant content, vol-%	6	15	25
Viscosity of extraction solution, cP	2,7	3,3	4,2
Cu content of raffinate, g/l	0,3	0,2	0,4
Rise in Cu content of extraction solution, g/l		3,7	4,9
Rise in Cu content of electrolyte, g/l	8,5	14	15,5
Rich electrolyte content, g/l	42,5	50	51,5
Ext. solution pumping ratio in extraction O/A	1,2	0,35	0,24
Ext. solution pumping ration in stripping O/A	8,5	3,8	3,2
Flow ratio of electrolyte and PLS	0,14	0,09	0,08

From this table the advantages given by our invention are apparent. In addition to the raised viscosity of the extraction solution and the fact that the solutions can be separated cleanly, it has been possible to reduce essentially the size of the equipment for handling the extraction solution in the extraction process, such as washing and stripping equipments, as well as oth r extraction solution equipment for the external circulation of the extraction solutions. Likewise the size of the equipment for the equipment for handling the electrolyte is reduced, such as flotation and pressure filtration apparatus, any possiblic post-separators and storage tanks. Another important factor is that the copp r content can be raised, ensuring the quality of the copper.

15

Example 3

In this example the performance values according to the prior art are shown in diagram 5 and the values of the method according to the present invention in diagrams 6 and 7, based on the presented stage calculations. These again show that the method helps reduce the size of the equipment considerably. The copper content of the aqueous solution is 3 g/l, i.e. still a dilute solution. The extractant content of an ordinary solution, given first in the table, is 8.5 vol.% and the following 15 and 25 vol.% according to this invention, as in the pr vious example. The extractant and diluting agent us d are the sam as in xample 2. The temperature of the extraction solution is 18 °C.

16

Table 3

Quantity	Kuva 5	Kuva 6	Kuva 7
Extractant content, vol-%	8,5	15	25
Viscosity of extraction solution, cP	3	3,3	4,2
Cu content of raffinate, g/l	0,3	0,25	0,35
Rise in Cu content of extraction solution, g/l	2,4	4,5	6,3
Rise in Cu content of electrolyte, g/l	9,5	14	15,5
Rich electrolyts content, g/l	45,5	50	51,5
Ext. solution pumping ratio in extraction O/A	1,13	0,61	0,42
Ext. solution pumping ration in stripping O/A	3,56	3,11	2,46
Flow ratio of electrolyte and PLS	0,29	0,2	0,17

5 Example 4

In this example, an aqueous solution was used with a Cu content of 6.5 g/l, in other words richer than is usually achieved with direct leaching of any poor ore. However, even when treating this kind of solution our method has distinct advantages. In the next table the stage calculations of diagrams 8, 9 and 10 were used. The contents of the extraction solution are 22, 30 and 40 vol.%, the extractant Acorga M6540 and the diluting agent again kerosene D70. The temperature of the extraction solution was 18 °C.

Table 4

Quantity	Fig. 8	Fig. 9	Fig. 10
Extractant content, vol-%	22	30	40
Viscosity of extraction solution, cP	3,7	4,9	6,3
Cu content of raffinate, g/l	0,2	0,3	0,4
Rise in Cu content of extraction solution, g/	5,9	9,2	14,5
Rise in Cu content of electrolyte, g/l	16	16	16
Rich electrolyte content, g/l	52	52	52
Ext. solution pumping ratio in extraction O/A	1,07	0,67	0,42
Ext. solution pumping ration in stripping U/A	2,71	1,74	1,1
Flow ratio of electrolyte and PLS	0,4	0,39	0,38

15

20

Example 5

This example studied the possibility of reducing the xternal pumping of the xtraction solution considerably by raising its extractant content t a significantly high I vel. When the pH of the base solution is close to 2 and the

same aqueous solution contains sulphates, the xtraction equilibrium is very beneficial when the copper content of the aqueous solution is low. In the cas of the example the Cu content of the aqueous solution is 2.5 g/l, the pH is 1.8 and the amount of sulphates 50 g/l. According to this example the method of

5 the present invention increases the copper extraction yield. As shown by the stage calculation in Fig.11, a very low raffinate content of 0.15 g/l copper is obtained while the external pumping of the extraction solution ratio drops to as low as 0.15. The external pumping of the electrolyte in ratio to the external pumping of the PLS also settles at the same value of 0.15. In this example the extractant used was the commercial chemical LIX 984N, which is similar to th reagent used in the previous example, and again kerosene D70 was th diluting agent. The extractant content was 50 vol.%.

Table 5

cuanety	Fig. 11
Viscosity of extraction solution, cP	8
Cu content of rafinate, g/l	0,15
Rise in Cu content of extraction solution, g/l	15,7
Rise in Cu content of electrolyte, g/	16
Rich electrolyte content, g/l	52
Ext. solution pumping ratio in extraction O/A	0,15
Ext. solution pumping ration in stripping O/A	1,02
Flow ratio of electrolyte and PLS	0,15

15

Example 6

The example shows how high the copper content of the PLS can be raised using our invention. In this example the Cu content of the PLS was raised up to 32 g/l while the extractant content of the extraction solution was raised to 50 vol.%, with Acorga M5640 as reagent and kerosene D70 as diluting agent. Mixing with the double helix mixer mentioned above is successful, even though an extractant content of as much as 40 - 70 vol.% is used. It is advantageous to do this when it is desired to reduce xternal pumping of th extraction solution. The stage calculation concerning 50 vol.% in Fig.12 and the summary in Table 6 clarify these possibilities further.

20

, ,

:

, s

.

.

•

Table 6

Quantity	Fig. 12	
Viscosity of extraction solution, cP	8,2	
Cu content of rafinate, g/l	5	
Rise in Cu content of extraction solution, g/l	. 13	
Rise in Cu content of electrolyte, g/l	16,5	
Rich electrolyte content, g/l	50,5	
Ext. solution pumping ratio in extraction O/A	2,07	
Ext. solution pumping ration in stripping O/A	1,27	
Flow ratio of electrolyte and PLS	1,63	

5

•. . . : . . 4 . · · , . . ٠. . . • . **`**; . . • ۰, . -

19

PATENT CLAIMS

- A method for extraction of copper from an aqueous solution containing a large amount of sulphates in liquid-liquid extraction, characterized in that the viscosity of an extraction solution is adjusted within the range of 3 –11 cP and that the volumetric ratio of the extraction solution and an aqueous solution in an extraction mixture to between 0.7 – 1.0, whereby th aqueous solution is dispersed into drops in the extraction solution.
- 10 2. A method according to claim 1, characterized in that the viscosity of the extraction solution is raised by raising the content of an extractant.
 - 3. A method according to claim 2, **characterized in** that the viscosity of the extraction solution is raised by regulating the extractant content of th extraction solution in the range of 15 70 vol. %.
 - 4. A method according to claim 1, characterized in that the ratio (O/A) between the organic solution and the aqueous solution coming to the extraction stage from outside is regulated in the range of 0.15 1.
- 20

15

5

5. A method according to claim 3, characterized in that in treating an aqueous solutions with a copper content of maximum 2 g/l, the viscosity of the extraction solution is raised by adjusting the content of the extractant in the extraction solution to the range of 15 – 25 vol.%.

25

30

6. A method according to claim 5, characterized in that the external pumping ratio of the extraction solution and the aqueous solution is adjusted to the range of 0.2 - 0.5 and the corresponding external pumping ratio between a stripped copper electrolyte and th aqueous solution of the extraction is adjusted to the rang of 0.08 - 0.02.

5

10

15

20

25

1

30

PCT/FI00/00397

- 7. A method according to claim 3, characteriz d in that in tr ating an aqueous solution with a copper content of 2 4 g/l, the viscosity of the extraction solution is raised by adjusting the content of the extractant in the extraction solution to the range of 15 30 vol.%.
- 8. A method according to claim 7, characterized in that the external pumping ratio of the extraction solution and the aqueous solution is adjusted to the range of 0.3 0.7 and the corresponding external pumping ratio between the stripped copper electrolyte and the aqueous solution of the extraction is adjusted to the range of 0.15 0.25.
- 9. A method according to claim 3, characterized in that in treating an aqueous solution with a copper content of 4 8 g/l, the viscosity of th extraction solution is raised by adjusting the content of the extractant in th extraction solution to the range of 25 50 vol.%.
- 10. A method according to claim 9, characterized in that the external pumping ratio of the extraction solution and the aqueous solution is adjusted to th range of 0.4 0.8 and the corresponding external pumping ratio between the stripped copper electrolyte and the aqueous solution of the extraction is adjusted to the range of 0.25 0.50.

11. A method according to claim 3, characterized in that in treating an aqueous solution with a copper content of over 8 g/l, the viscosity of th extraction solution is raised by adjusting the content of the extractant in th extraction solution to the range of 40 - 70 vol.%.

12. A method according to claim 11, characterized in that the external pumping ratio of the extraction solution and the aqueous solution is adjust d within the range of 1 - 4 and the corresponding xt rnal pumping ratio between the stripped copper electrolyte and the aqueous solution of

the extraction is adjusted within the range of 0.8 - 3.

13. A method according to claim 1, characterized in that the viscosity of the extraction solution is raised by using alifatic hydrocarbons, kerosenes, with a viscosity of 2.7 – 3.2 cP when measured at ambient temperature, as diluting agent for the extraction solution.

14. A method according to claim 1, **characterized in** that the viscosity of the extraction solution is raised by using aromatic hydrocarbons, kerosenes, with a viscosity of about 3 cP when measured at ambient temperature, as diluting agent for the extraction solution.

15. A method according to any of the above claim, **characterized in** that the viscosity of the extraction solution is raised by using a mixture of alifatic and aromatic hydrocarbons, with a viscosity of minimum 2.7 cP when measured at ambient temperature, as diluting agent for the extraction solution.

* E - 17

16. A method according to claim 1, characterized in that the sulphate cont at

of the aqueous solution fed to solvent extraction is minimum 40g/l.

20

15

17. A method according to any of the above claim, characterized in that the

extracting solutions flow through each stage of the extraction equipment at essentially the same time.

25

18. A method according to any of the above claim, characterized in that the extracting solutions flow through the washing and stripping stages of the equipment more slowly than the actual extracting stages.

10

1

ł. •

·····

: . .

-•••

. · ·

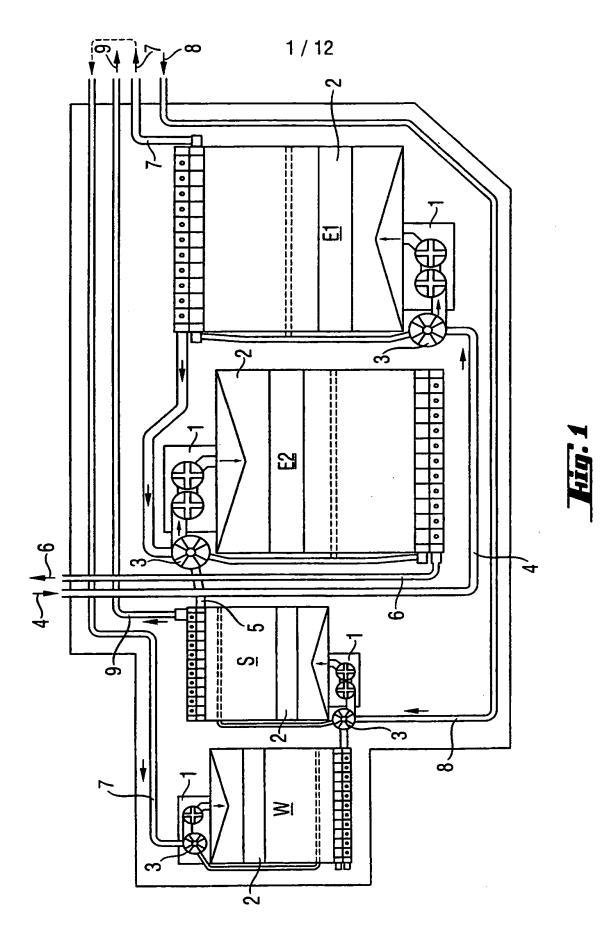
•

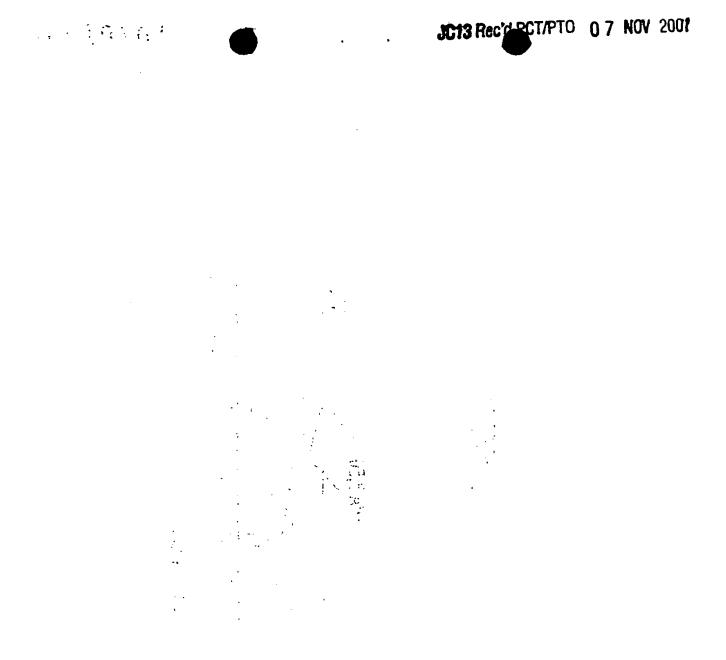
• :

z

10/019967

PCT/FI00/00397



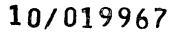


•

. . . .

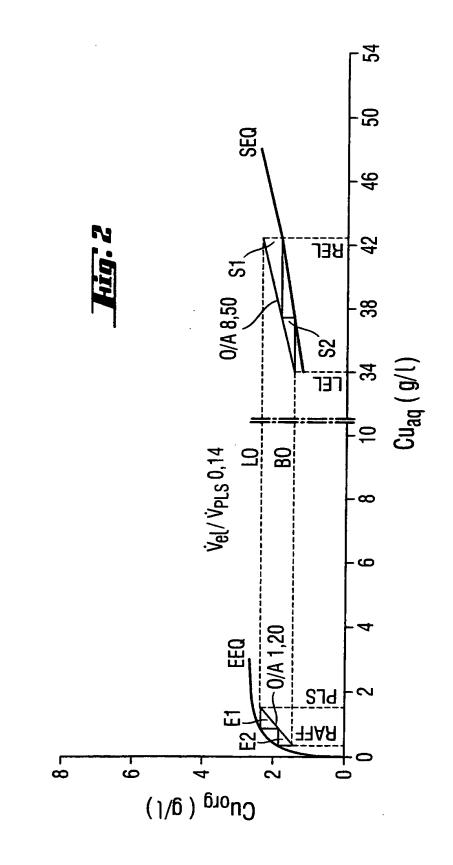
.

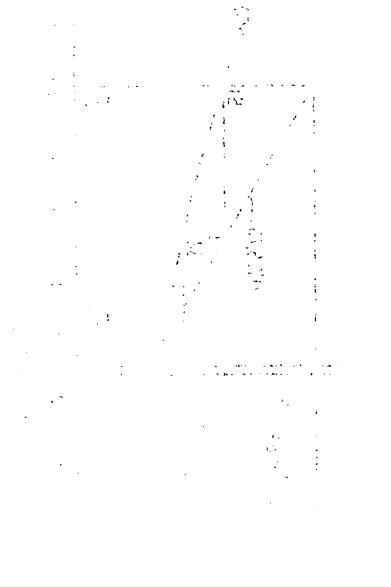
:



PCT/FI00/00397

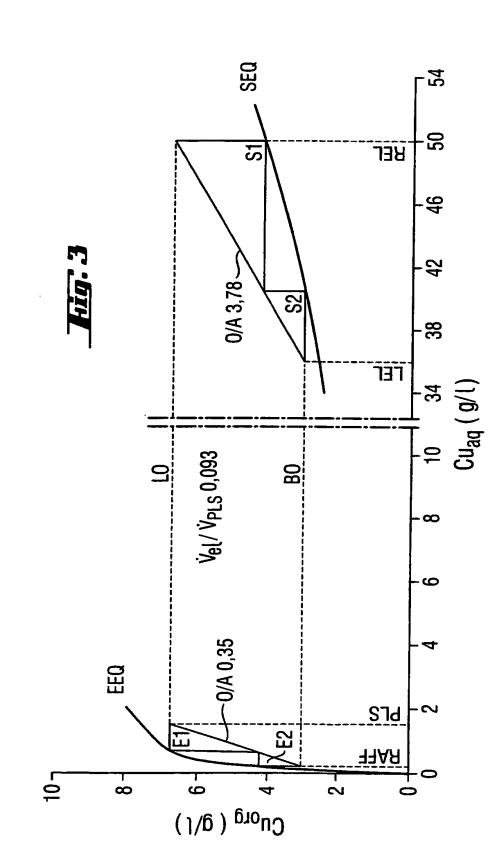






.

•



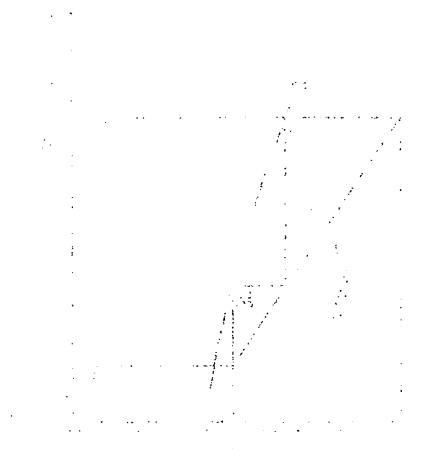
٠

- ,

3 / 12

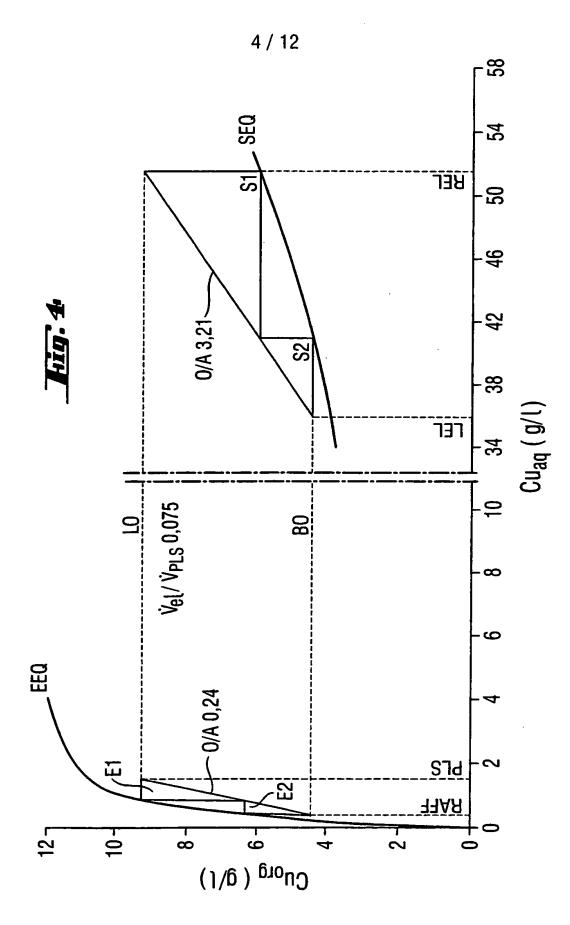
10/019967

.



. · · · ·

. .



-

PCT/FI00/00397

10/019967

.

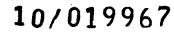
· .

. : . .

.

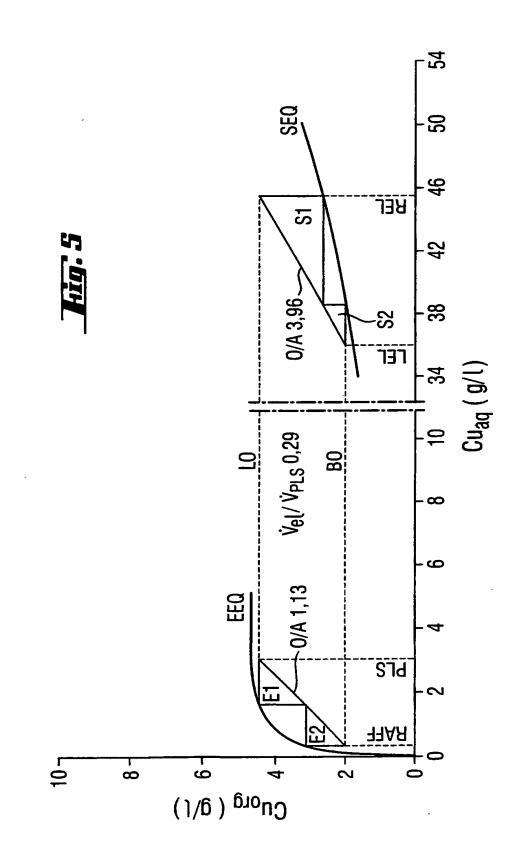
JC13 Rec'd PCT/PTO 0 7 NOV 2001

•



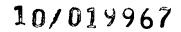
PCT/FI00/00397







.

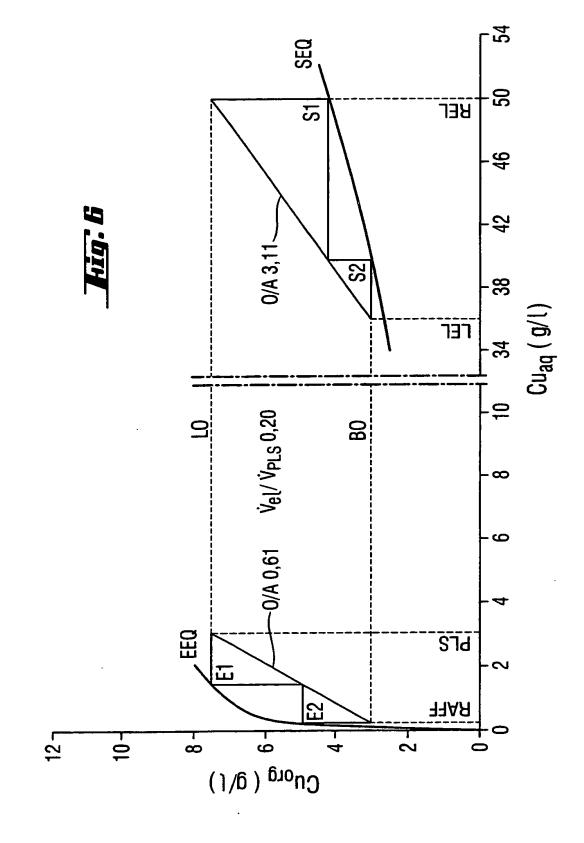


PCT/F100/00397

•

7 1





.



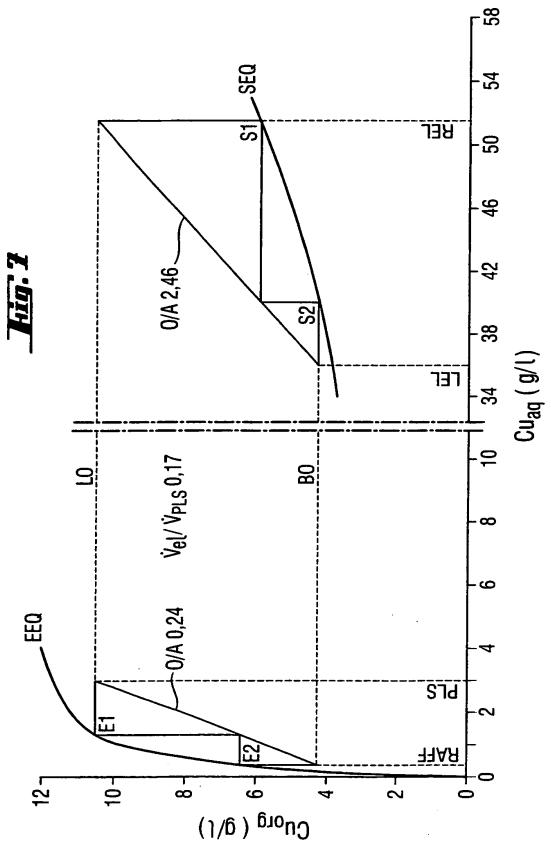
na serie de la construcción de la c La construcción de la construcción d La construcción de la construcción d

1

10/019967

·

PCT/FI00/00397



7 / 12

.

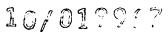
•



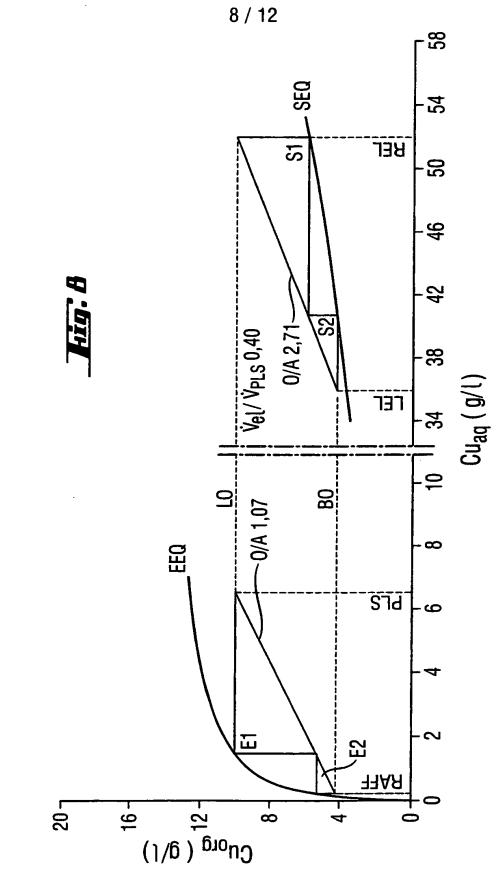
1 i 1

•





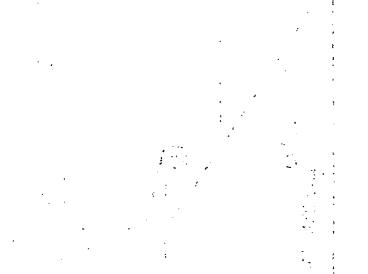
PCT/FI00/00397



-

•







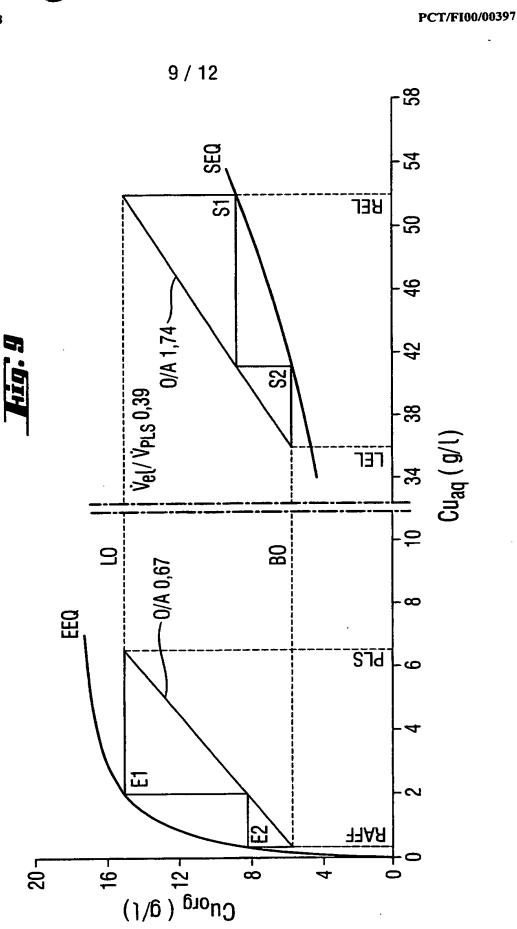






JC13 ROCH PCT/PTO 07 NOV 2001

٠,



.

10/019967

.

.







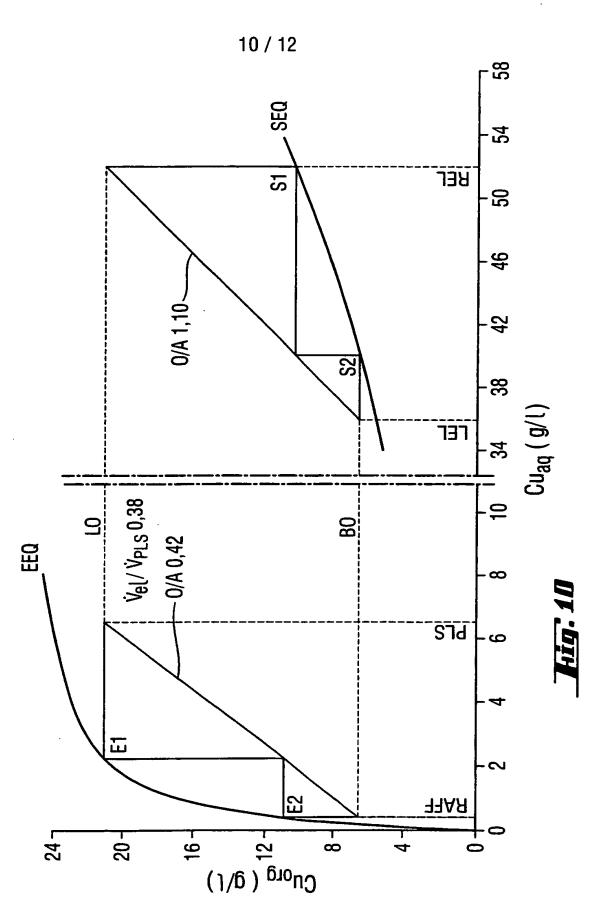
· · · ·

. .

.

JC13 Per'd PCT/PTO 0 7 NOV 2001

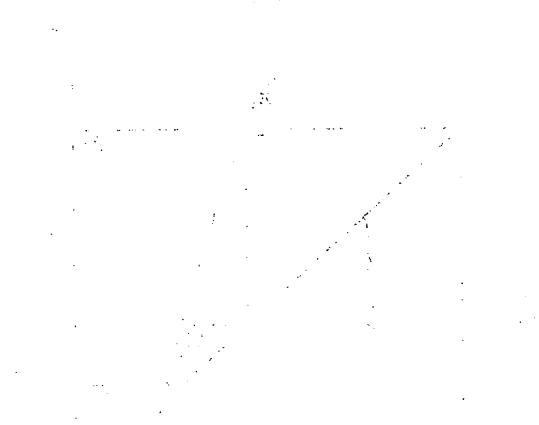
•



ì

PCT/FI00/00397

10/019967



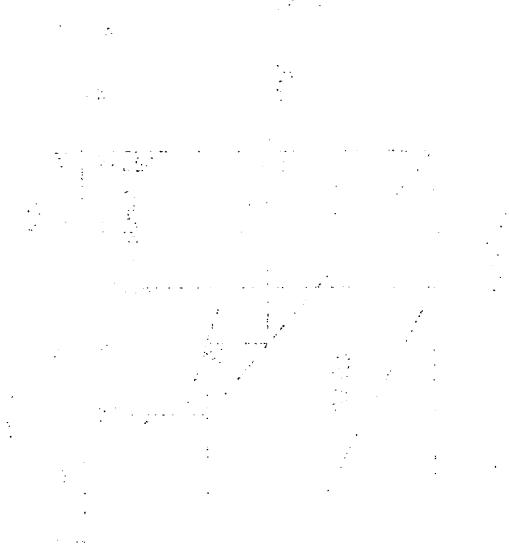
.

10/019967 PCT/F100/00397 WO 00/69538 11 / 12 58 SEQ 54 13A <u>S1</u> 50-46 0/A 1,02~ Hig. 11 42 S2 38. Cu_{aq} (g/l) TET 34 2 Ýel∕ Ý_{PLS} 0,15 2 8 ∞ EEQ <u>ں</u> 0/A 0,15 STJ -~ <u>ы</u> ш **AAFF** ي Cu_{org} (g/l) 8 24 J 20-16-0

4

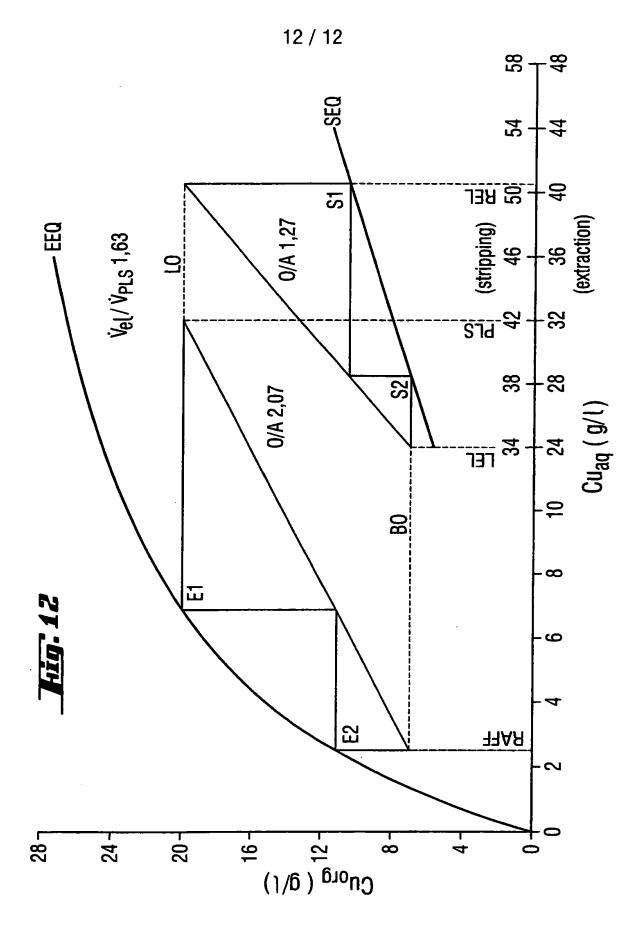
۵,

ć



10/019967

PCT/FI00/00397



M PCT/PTO 07 NOV 2001

· · · · · . . .

a a companya a A companya a

م زیر الحجار کے الحج میں الائی کی۔ الحجاج · •

a da entre esta esta esta esta esta en la composición de la c ł · .

.

S. A. A. State of the State

.

.

. .

.

• · · · . , . -

.

· ·

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00397

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B01D 11/04, C22B 3/26 // C22B 15:00 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B01D, B01F, C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ, EDOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category* Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.
X GB 2117666 A (UNIVERSITY OF MAN OF SCIENCE AND TECHNOLOGY), (19.10.83), claims 1,9, ab	19 October 1983	1-18
X US 4221658 A (WILLIAM E. HARDWI (09.09.80), claims 1-2	CK), 9 Sept 1980	1-18
A US 5662871 A (BROR NYMAN ET AL) (02.09.97), abstract	, 2 Sept 1997	1-18
A US 5185081 A (BROR G. NYMAN ET 9 February 1993 (09.02.93), abstract		1-18
Further documents are listed in the continuation of Box	C. X See patent family annex.	
 Special categories of cited documents; "A" document defining the general state of the art which is not considered 	"T" later document published after the inter date and not in conflict with the applic the principle or theory underlying the in	ation but cited to understand
to be of particular relevance "E" erlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other	"X" document of particular relevance: the c considered novel or cannot be consider step when the document is taken alone	laimed invention cannot be
 special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means 	"Y" document of particular relevance: the c considered to involve an invenue step combined with one or more other such	when the document is documents, such combination
"P" document published prior to the international filing date but later than the priority date claimed	being obvious to a person skilled in the "&" document member of the same patent f	
Date of the actual completion of the international search	Date of mailing of the international se	arch report
11 Sept 2000	15 -09- 2 000	
Name and mailing address of the ISA/	Authorized officer	
Swedish Patent Office		
Box 5055, S-102 42 STOCKHOLM	Lars Ekeberg/MP	
Facsimile No. + 46 8 666 02 86	Telephone No. + 46 8 782 25 00	

Form PCT/ISA/210 (second sheet) (July 1992)



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No. 08/05/00 PCT/FI 00/00397 .

				08,	/05/00	PCI/FI	00/0039/
	nt document n search report		Publication date	P	atent family member(s)		Publication date
GB	2117666	A	19/10/83	NONE			
US	4221658	A	09/09/80	AU	33415	78 A	30/08/79
				BE		32 A	16/06/78
				BR	78010		02/01/79
				CA	10942		27/01/81
				DE	28071	29 A	24/08/78
				FR	24180		21/09/79
				GB	16015		28/10/81
				SE	78018		22/08/78
				ZA	78009		28/02/79
				ZM	19	78 A	21/11/78
US	5662871	A	02/09/97	AU	6862	50 B	05/02/98
				AU	78893	94 A	15/06/95
				BR	94048	33 A	01/08/95
				CA	21371		03/06/95
				CN	10505	22 B	22/03/00
				CN	11109		01/11/95
				FI	969	68 B,C	14/06/96
				FI	9353	93 A	03/06/95
				ZA	94091	33 A	24/07/95
US	5185081	A	09/02/93	AU	6385	62 B	01/07/93
			-	AU	73951	91 A	10/10/91
				CA	20396	76 C	06/12/94
				FI	887	73 B,C	31/03/93
				FI	9016		05/10/91
				MX	1732	25 B	09/02/94
				TR	264	67 A	15/03/95

 $\langle \cdot \rangle$

leceivad	1 B			WO 00/69538 PCT/FI00/0039
3 0. 11. 🗇 PAT	ENT COOPE	RATION TREA	TY	
	k			
PCT NOTICE INFORMING THE API COMMUNICATION OF THE II APPLICATION TO THE DESIG (PCT Rule 47.1(c), first	NTERNATIONAL NATED OFFICES	To: OUTOKUMPU Patent Service P.O. Box 27 FIN-02201 Esp FINLANDE	es	
Date of mailing (day/month/year) 23 November 2000 (23.11.00))	<u>]</u> [
Applicant's or agent's file reference 991111 WO		41	MPORTANT NOTICE	
International application No. PCT/FI00/00397	-	date (day/month/year) 00 (04.05.00)	Priority date (day/month/ 14 May 1999 (14.	
AU,KP,KR,US In accordance with Rule 47.1(c), third the communication of the internation of the international application is requ 2. The following designated Offices hav AE,AL,AM,AT,AZ,BA,BB,BC HR,HU,ID,IL,IN,IS,JP,KE,KG RO,RU,SD,SE,SG,SI,SK,SL, The communication will be made to t applicant to furnish a copy of the inte 3. Enclosed with this Notice is a copy of 23 November 2000 (23.11.00) under the	al application has duly vired to be furnished b e waived the requirem G,BR,BY,CA,CH,CN ,KZ,LC,LK,LR,LS,L TJ,TM,TR,TT,UA, hose Offices only upoi rnational application (the international appli	v taken place on the date wy the applicant to the demonstrain N,CU,CZ,DE,DK,EA,E LT,LU,LV,MD,MG,MI UG,UZ,VN,YU,ZA,ZV n their request. Furtherm Rule 49.1 (a-bis)).	of mailing indicated above signated Office(s). cation at this time: E,EP,ES,FI,GB,GD,GE K,MN,MW,MX,NO,NZ W ore, those Offices do not re	e and no copy E,GH,GM, Z,PL,PT, equire the
REMINDER REGARDING CHAN If the applicant wishes to postpone er date, a demand for international preli Examining Authority before the expir It is the applicant's sole responsibility Note that only an applicant who is a r right to file a demand for internationa REMINDER REGARDING ENTI If the applicant wishes to proceed wit or 30 months, or later in some Offices For further important information on t Annex to Form PCT/IB/301 (Notification	Attry into the national p minary examination m ation of 19 months from to monitor the 19-mon ational or resident of a preliminary examinat RY INTO THE NAT In the international app perform the acts refe he time límits and acts	hase until 30 months (or nust be filed with the com m the priority date. Inth time limit. a PCT Contracting State v tion. IONAL PHASE (Artic plication in the national p prred to therein before ea s to be performed for ent	later in some Offices) from petent International Prelim which is bound by Chapter c le 22 or 39(1)) hase, he must, within 20 m ch designated or elected O ering the national phase, so	ninary Il has the ionths Office.
The International Bureau of 34, chemin des Colombe 1211 Geneva 20, Switzer	ttes	Authorized officer	J. Zahra	

Telephone No. (41-22) 338.83.38

Facsimile No. (41-22) 740.14.35 Form PCT/IB/308 (July 1996)

2

3661535

.

.

. .

PATENT	COOPER	ATION	TRE
--------	--------	-------	-----

From the INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Outokumpu OYJ	Intellectual
Property Manag	jement
P.O. Box 27	
FIN-02201 Espo	00
Finland	

PCT

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

·		(day/month/year)	01-06-2001	
Applicant's or agent's file reference 991111 WO	e	ІМРС	DRTANT NOTIFICATION	
International application No. PCT/FI00/00397	International filing dat 04-05-20		Priority date (day/month/year) 14-05-1999	
Applicant Outokumpu Oyj et al				

Date of mailing

- 1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
- 2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- 3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in som Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary axamination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/		Authorized officer	
Patent- och registreringsverket Box 5055	Telex 17978 PATOREG-S	Ihla Rönnberg	
S-102 42 STOCKHOLM Facsimile No. 08-667 72 88		Telephone No. 08-782 25 00	

Form PCT/IPEA/416 (July 1992)

e e e e en en en se se se s

· ... ·

•

· · · · · · · · ·

· · · ·

.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	<u></u>	See Notifi	cation of Transmittal of International
991111 WO	FOR FURTHER ACTION	N	ry Examination Report (Form PCT/IPEA/416)
International application No.	International filing date (day	/month/year)	Priority date (day/month/year)
PCT/F100/00397	04.05.2000		14.05.1999
International Patent Classification (IPC) o	r national classification and IP	°C7	
B01D 11/04, C22B 3/26			
Annlieget	······································		
Applicant Outokumpu Oyj et al			
ouconumpu oyj et ar			
1. This international preliminary exe Authority and is transmitted to th	amination report has been prep a applicant according to Articl	ared by this Inte le 36.	mational Preliminary Examining
-			r sheet
2. This REPORT consists of a total	•		
been amended and are the	basis for this report and/or she	ets containing re	tion, claims and/or drawings which have ectifications made before this Authority
(see Rule 70.16 and Section	n 607 of the Administrative In	structions under	the PCT).
These annexes consist of a total of	of		
· · · · · · · · · · · · · · · · · · ·			· · · · · · · · · · · · · · · · · · ·
3. This report contains indications re	elating to the following items:		
I Basis of the report			
II Priority			
III Non-establishment o	of opinion with regard to novel	ty, inventive ste	p and industrial applicability
IV Lack of unity of invo	ention		
V Reasoned statement	under Article 35(2) with regar	d to novelty, inv	ventive step or industrial applicability;
citations and explana	ations supporting such stateme	nnt	
VI Certain documents o			
	e international application		
VIII Certain observations	s on the international application	m	
			······································
Date of submission of the demand	Da	ate of completion	n of this report
29.11.2000	1	5.05.200	1
Name and mailing address of the IPEA/S	SE AI	uthorized officer	г
Patent- och registreringsverket	Telex 17978		
Box 5055 S-102 42 STOCKHOLM	PATOREG-S L	ars Ekeb	
Encouvile No. 08-667 72 88	l Te	elephone No. 06	8-782 25 00

Facsimile No. 08-667 72 88 Form PCT/IPEA/409 (cover sheet) (January 1998)

• • • •

. · -.

- • .
- • • · · · · · · . i
 - 1. A. 1977
- •
- - , A set of the set o ,
- · •
- · . • • • • • • • • • • • ----
- · •

- and a start of the start of the start of the start. A start of the start
 -

 - .
 - and the second second
 - · · · · • · ,

 - • . · · ·
 - •
 - •



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00397

	the report	
	d to the elements of the international	
the the	international application as originally	filed
the	description:	1. 51. 1
pag	es	, as originally filed
pag	es	, filed with the demand
pag	es	, filed with the letter of
the	claims:	, as originally filed
pag	es	, as originally filed
pag		, as amended (together with any statement) under article 19 , filed with the demand
pag	es	, filed with the letter of,
	drawings:	, as originally filed
		filed with the demand
. pag	2es	, tiled with the letter of
	sequence listing part of the description	
	ies	, as originally filed
		, filed with the demand
P**C	Jes	, filed with the letter of
These eler the	ational application was filed, unless of ments were available or furnished to t clanguage of a translation furnished for clanguage of publication of the intern	this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). hational application (under Rule 48.3(b)).
These elect the the the or	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3).	this Authority in the following language
These elea the the the or With rega	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the	therwise indicated under this item. this Authority in the following language
These elect the the the the or With rega prelimina	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the intained in the international application	this Authority in the following language
These elect the the the or With rega prelimina	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the intained in the international application ed together with the international application	therwise indicated under this item. this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). A for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: on in written form. Solication in computer readable form.
These elect the the the or With rega prelimina con fill fun	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the intained in the international application ed together with the international appli- mished subsequently to this Authority	this Authority in the following language
These elect the the the the or With rega prelimina con file	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a vry examination was carried out on the ntained in the international application ed together with the international appli- rmished subsequently to this Authority	therwise indicated under this item. this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). A for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: m in written form. blication in computer readable form. y in computer readable form.
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a vry examination was carried out on the intained in the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority	this Authority in the following language
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the intained in the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority to statement that the subsequently fur	therwise indicated under this item. this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). A for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: on in written form. blication in computer readable form. y in computer readable form. y in computer readable form. inished written sequence listing does not go beyond the disclosure in the one formiched
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the intern e language of the translation furnished 55.3). ard to any nucleotide and/or amino a try examination was carried out on the intained in the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority to statement that the subsequently fur	this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). national application (under Rule 48.3(b)). If for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: on in written form. blication in computer readable form. y in computer readable form. nished written sequence listing does not go beyond the disclosure in the
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a ary examination was carried out on the intained in the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority to statement that the subsequently fun- temational application as filed has been the statement that the information recor- tion furnished.	therwise indicated under this item. this Authority in the following language which is for the purposes of international search (under Rule 23.1(b)). A for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: on in written form. blication in computer readable form. y in computer readable form. inished written sequence listing does not go beyond the disclosure in the en furnished. orded in computer readable form is identical to the written sequence listing has
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a ury examination was carried out on the intained in the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority mestatement that the subsequently furnite mational application as filed has been the statement that the information recor- tion furnished.	therwise indicated under this item. this Authority in the following language
These elect	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the interne e language of the translation furnished 55.3). and to any nucleotide and/or amino a very examination was carried out on the ntained in the international application ed together with the international appli- mished subsequently to this Authority mished subsequently to this Authority to statement that the subsequently fun- ternational application as filed has been be statement that the information recor- tion furnished. the amendments have resulted in the car- the description, pages	this Authority in the following language
These elect	ational application was filed, unless or ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a vry examination was carried out on the intained in the international application ed together with the international application ed together with the international application mished subsequently to this Authority rnished subsequently to this Authority to statement that the subsequently fun- temational application as filed has been be statement that the information recor- ten furnished. The amendments have resulted in the ca- the description, pages the claims, Nos.	of the revise indicated under this item. this Authority in the following language which is For the purposes of international search (under Rule 23.1(b)). which is actional application (under Rule 48.3(b)). d for the purposes of international preliminary examination (under Rules 55.2 and/ actional sequence disclosed in the international application, the international e basis of the sequence listing: m in written form. olication in computer readable form. y in computer readable form. nished written sequence listing does not go beyond the disclosure in the teen furnished. rdeed in computer readable form is identical to the written sequence listing has ancellation of:
These elect	ational application was filed, unless or ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a vry examination was carried out on the intained in the international application ed together with the international application ed together with the international application mished subsequently to this Authority rmished subsequently to this Authority to statement that the subsequently fun- ternational application as filed has been be statement that the information recor- tion furnished. the amendments have resulted in the ca- the claims, Nos. the drawings, sheet/fig	offerwise indicated under this item. this Authority in the following language
These elect the the the the or With regas prelimina ful ful ful ful ful ful ful ful ful ful	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a try examination was carried out on the ntained in the international application ed together with the international application ed together with the international application mished subsequently to this Authority mished subsequently to this Authority ternational application as filed has been the statement that the subsequently furn ternational application as filed has been the description, pages the claims, Nos. the drawings, sheet/fig his report has been established as if (s eyond the disclosure as filed, as indice	which is: this Authority in the following language
These elect the the the the the the the th	ational application was filed, unless of ments were available or furnished to t e language of a translation furnished for e language of publication of the interne- e language of the translation furnished 55.3). and to any nucleotide and/or amino a vry examination was carried out on the ntained in the international application ed together with the international application ed together with the international application mished subsequently to this Authority rnished subsequently to this Authority to the statement that the subsequently fun- temational application as filed has been the estatement that the information recor- tion furnished. The description, pages the claims, Nos. the drawings, sheet/fig his report has been established as if (se eyond the disclosure as filed, as indica- tement sheets which have been furnished report as "originally filed" and are an 17).	this Authority in the following language which is. For the purposes of international search (under Rule 23.1(b)). A for the purposes of international preliminary examination (under Rules 55.2 and/ acid sequence disclosed in the international application, the international e basis of the sequence listing: on in written form. Mication in computer readable form. y in computer readable form. nished written sequence listing does not go beyond the disclosure in the en furnished. orded in computer readable form is identical to the written sequence listing has ancellation of:

•

•

and the second

•

.

· · · · ·

. .



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00397

citations and explanations suppor		
 Statement	•	
Novelty (N)	Claims Claims	<u>1-18</u> NO
Inventive step (IS)	Claims Claims	<u>1-18</u> NC
Industrial applicability (IA)	Claims Claims	<u>1-18</u> NO
Citations and explanations (Rule 7). 7)	
viscosity of the ex The between the ex is situated between	straction stract	
The following dod International Sear D1: GB 2 117 666 A D2: US 4,221,658 A D3: US 5,662,871 A D4: US 5,185,081 A	ch Repo	- , -
represent the gene	ce, white ral state report. luated.	lle D3 and D4 only were considered to ate of the art, and are therefore not However, the importance of D1 and D2 They are now only considered to
From D1, a method	for hy	drometallurgical extraction of copper ween the extraction solution and the erably situated around 1.0 (claim 9).
the preferred vo. Nothing is, on th	lume ra ne othe documen he visc	d is known from D2. In both D1 and D2 atio is situated between 0.2 and 5. r hand, said about the viscosity, in ats. It is not suggested that an cosity could have a positive influence
		/
		•

· ·

- i
- i

. . ••• •

... ·

•

. •

•

. •

.



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00397

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: BOX V (I)

Although it is difficult to estimate the viscosity of the solutions used in D1 and D2, the invention is considered to involve an inventive step with regard to both of these documents. Claims 2 -18 are dependent on the first claim, hence, these claims are also considered to possess an inventive step.

In view of the argument stated above, the invention as a whole is novel and considered to involve an inventive step. It is also considered to fulfil the criteria of novelty and industrial applicability.

a mana tanàna mandritra dia kaominina dia kaominina dia kaominina dia kaominina dia kaominina dia kaominina dia (1) Some start and the second start of the the two second second states in the second and the second secon $\phi \in \mathcal{Y}^{\infty}(M)$ and $\phi \in \mathcal{Y}^{\infty}(M)$ is the set of $\phi \in \mathcal{Y}^{\infty}(M)$ is the set of $\phi \in \mathcal{Y}^{\infty}(M)$ is the set of ϕ For the second se Second se the second s ·. $\mathbf{x}_{1} = \mathbf{x}_{1} + \mathbf{x}_{2} + \mathbf{x}_{2} + \mathbf{x}_{3} + \mathbf{x}_{4} + \mathbf{x}_{4}$ • • • • .. <u>.</u> • .